

FINAL REPORT TO NASA

Titles: Thermal Protective Coating for High Temperature Polymer Composites

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PROJECT DESCRIPTION

The central theme of this research is the application of carboxylate-alumoxane nanoparticles as precursors to thermally protective coatings for high temperature polymer composites. In addition, we will investigate the application of carboxylate-alumoxane nanoparticle as a component to polymer composites.

Research Objectives and Expected Significance.

The objective of this research was the high temperature protection of polymer composites via novel chemistry. The significance of this research is the development of a low cost and highly flexible synthetic methodology, with a compatible processing technique, for the fabrication of high temperature polymer composites. We proposed to accomplish this broad goal through the use of a class of ceramic precursor material, alumoxanes. Alumoxanes are nano-particles with a boehmite-like structure and an organic periphery.

The technical goals of this program are to prepare and evaluate water soluble carboxylate-alumoxane for the preparation of ceramic coatings on polymer substrates.

Our proposed approach is attractive since proof of concept has been demonstrated under the NRA 96-LeRC-1 Technology for Advanced High Temperature Gas Turbine Engines, HITEMP Program. For example, carbon and Kevlar® fibers and matting have been successfully coated with ceramic thermally protective layers.

Background and Prior Results

Carboxylate-alumoxanes are prepared from the reaction of boehmite, $[\text{Al}(\text{O})(\text{OH})]_n$, with carboxylic acids (HO_2CR). Although, they are given the general formula, $[\text{Al}(\text{O})_x(\text{OH})_y(\text{O}_2\text{CR})_z]_n$ where $2x + y + z = 3$ and $R = \text{C}_1 - \text{C}_{14}$,¹ carboxylate-alumoxanes are in fact alumina nano-particles between 5 - 200 nm in diameter. The surface of the nano-particle is covered with covalently bound carboxylate groups. The physical properties of the alumoxanes are highly dependent on the identity of the alkyl substituents, R, and solutions water soluble alumoxanes are readily formed with polyether ligands.²

The parent alumoxanes yield γ -alumina upon very mild thermolysis with a subsequent low temperature conversion to α -alumina. However, alkaline earth, transition metal and lanthanide hexaluminates may also be prepared by a unique room temperature metal exchange reaction.³ The reaction of solutions of the carboxylate-alumoxane with simple inorganic complexes yields metal-doped carboxylate-alumoxanes from which the mixed metal oxides are formed upon thermolysis.

We have previously shown that dip coating a variety of substrates into aqueous or hydrocarbon solutions of the carboxylate-alumoxane allows for a uniform coating with no cracking or spallation. These carboxylate-alumoxane coatings may then be readily transformed to highly uniform continuous ceramic coatings at moderate temperature. We have demonstrated the coating of sapphire, SiC, graphite and most importantly Kevlar fibers in this manner.⁴

An indication of the oxidation protection provided by our carboxylate-alumoxane produced coatings to polymers is that our alumina coated Kevlar fibers have successfully been incorporated into alumina matrix composites, without significant loss in the strength of the fibers.

Research Report.

Task 1: Fabrication of Aluminate Coated Polymers. The broad goal of this task included: the development of a method to use carbon composites in high temperature applications and to increase the temperature at which the carbon composites can be used. In this regard the objective of this task was to identify conditions for coating organic polymer substrates with doped alumoxane preceramic oligomers. Our approach involved coating the carbon composites with an alumoxane derived alumina coating. We have used acetate-alumoxane (A-alumoxane) since it is water soluble and has a high ceramic yield (75 - 80%). We have previously found that 1% solutions provide the best coatings.⁴

Initial studies were aimed at determining the most effective coating conditions. Two solution concentrations of A-alumoxane (1 and 6 wt%) were studied. SEM images and elemental carbon and aluminum mapping were performed before and after heat treatment to 400 °C to determine the success of coating retention. For the composites coated with 1 wt% A-A, there was uniform coverage and the coating was almost entirely free of cracks before heat treatment. Elemental mapping shows that there is virtually no carbon showing. However, after firing, there now appears to have areas where spallation occurred. Elemental mapping of carbon and aluminum is consistent with this, showing that carbon is now present. When the composites were coated with 6 wt% A-A, even before firing, the surface coating is non-uniform. After firing, the coating is still non-uniform, however, it is more severe. Elemental mapping performed on the surface shows a higher level of carbon present for the fired samples. Thus, using the 1 wt% A-A solution to coat the composites produces a more uniform coverage before heat treatment compared to the higher 6 wt% solution.

TGA experiments were performed on the 1 and 6 wt% coated samples with identical results. When reviewing the TGA of the composite before application of any coating, it was noticed that there were 2 steps where burn-off occurred; first one was up to 200 °C which resulted in a weight loss of 1 % of total weight and the second was after 450 °C. Viewing the SEM images of a coated composite at 50 °C intervals showed that the coating was smooth and remained uniform until 200 °C.

The progression of the alumoxane coating was evaluated at various points along the coating process. A sample was dip coated in an aqueous 1% solution of A-alumoxanes and air dried. The coating showed no cracks or visible defect by SEM. No cracks were observed after heating the sample to 100 °C, however, at 200 °C significant cracking was observed. Given that A-alumoxane does not lose significant mass until 240 °C, the formation of cracks must be due to the evolution of volatiles from the composite. This is supported by the fact that additional damage to the coating is not observed upon heating to 400 °C. Thus, it is important to ensure that the composite has no volatiles prior to firing past 200 °C.

Coating retention is improved by heating the composites at 250 °C for 5 hours prior to coating, however spallation is still observed. As an alternative the carbon composites were heated under vacuum to 140 °C for 2 days prior to coating. This resulted in a 1 - 2 % mass loss, presumably due to water and other volatiles. However, if the samples are stored in air this mass is regained over a few days. Since we have previously found that water provided a good coating on carbon fibers,⁴ and our desire to maintain aqueous processing, we investigated vacuum drying, in a desiccator, the composites after each coating step. However, the SEM images indicated extensive cracking of the coating even prior to firing to 400 °C. This is found to be due to the increase the drying speed caused by the vacuum. Our prior results have shown that drying rate is important in

providing a continuous coating. The catastrophic presence of cracks was indicated by TGA experiments in air which showed a weight loss of 85% associated with combustion of the carbon composite. These results suggest that the water solvent for the alumoxane is being absorbed into the "dried" composite. This water is then being released above 100 °C and causing cracking of the alumoxane. These cracks are retained in the ceramic coating.

It is clear from our results that either a slower dry step is required possibly using reduced pressure (but not vacuum) or a more volatile solvent must be substituted that does not absorb into the composite. Therefore, we propose to investigate the suitability of various solvents by exposing dried composites to the solvent and measuring the TGA. We will also investigate the absorption process by solid state CPMAS ^{13}C NMR spectroscopy.

Task 2. Fabrication of Carbon Fiber/Alumoxane Based Resin Composites.

The objective of this task was to employ our previously characterized alumoxane-based epoxy resins as matrix materials in resin/carbon fiber composites.

Chemically functionalized alumina nanoparticles (carboxylate-alumoxanes) are used as the inorganic component of a new class of inorganic-organic hybrid materials. Lysine- or *para*-hydroxybenzoic acid-derivatized alumoxanes are readily prepared from the reaction of boehmite, $[\text{Al}(\text{O})(\text{OH})]_n$, with the appropriate carboxylic acid. The peripheral organic hydroxides and amines of these carboxylate-alumoxanes either react directly with epoxide resins, such as the diglycidyl ether of bisphenol-A (DER 332), to form a hybrid material, or in the presence of an organic resin and hardener system to form a composite material.⁵ A significant increase in thermal stability and tensile strength is observed for both the hybrid and composite resin systems. We have previously demonstrated that both carbon fiber and carbon/Kevlar® matting may be successfully incorporated into the hybrid resin systems resulting in further property improvements.

Two specific research goals were investigated: 1) the increase in physical strength of the fiber/resin composite, especially torsional stiffness and 2) the minimization of diffusion as measure by density. The former was investigated at Rice while the latter measurements were performed at NASA.

Two 15.5 cm x 15 cm flat aluminum molds were covered with aluminum foil. A thin layer of the mold release was brushed on to the foil and allowed to dry. Approximately, 14 cm x 11 cm carbon fabric pieces were cut out and treated with resin, alumoxane and hardener in the following manner.

A. Resin, hardener and alumoxane were mixed together using a mechanical stirrer. This mixture was brushed on to both sides of either 5 or 2 layers of carbon fabric.

B. Fabrics were dipped in a saturated solution of alumoxane and then allowed to drip dry. Resin and hardener were mixed together and brushed on to the carbon fabrics.

C. Fabrics were dipped in a saturated solution of Alumoxane. Resin and hardener were mixed together and brushed on to the wet carbon fabric pieces.

D. Fabrics were dipped in a saturated solution of alumoxane and then allowed to drip dry. Resin and hardener were dissolved in acetone and brushed on to the carbon fabrics.

The carbon fabric layers were clamped between two layers of the aluminum mold and then cured at 150 °C for 2 and 12 hours depending on the hardener. The SEM images are of small pieces that were cut out from the center of the composites. Methods involving a solvent often resulted in porous composites due to evaporation of the solvent.

Mechanical testing showed that the presence of alumoxane had a significant effect on the physical properties of the composite. In addition, the identity of the alumoxane was important. Two alumoxanes were investigated: lysine and *para*-hydroxybenzoate (*p*-HB) alumoxanes.

The tensile strength was increased with the alumoxane. Furthermore, lysine-alumoxane showed a greater increase (85,650 psi) than *p*-HB-alumoxane (77,060 psi). As may be expected the tensile strength increased with the increased alumoxane content (85,650 psi for 0.7% w/w versus 72,280 psi for 0.2% w/w lysine-alumoxane). Tensile strength is also increased by vacuum bagging although the modulus is not changed which does occur with the use of the alumoxanes). The shear strength is higher for lysine-alumoxane than *p*-HB-alumoxane and increased with the alumoxane content (7,590 psi with 0.7 %w/w versus 5,540 for 0.2%w/w). The compressive strength is not changed by the alumoxane but is affected by vacuum processing. In contrast to the other properties, *p*-HB increases flexural strength (90,860 psi) more than lysine-alumoxane (27,960 psi). The flexural strength is unaffected by vacuum.

We are continuing our physical testing of these materials especially with regard to the extent to which the alumoxane increases the torsional (flexural) strength.

References

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